

Fluorescence line narrowing (FLN), spectral hole-burning and slow light in natural and lab-grown emerald.

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The green variety of the ring silicate beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, is called emerald and its colour is caused by ca. 0.1–0.5 % Cr^{3+} substituting for the Al^{3+} ions in sites of D_3 point symmetry. The V^{3+} ion may also be present, and in principle can be the chromophore in both natural and lab grown emerald. Beryl crystallizes in the hexagonal space group $P6/mcc$ (W.A. Deer 1962) and is commonly found in vugs and druses within granite or granite pegmatites. Its natural occurrence is related to the accumulation of Be^{2+} ions in hydrothermal and residual magmatic fluids, as the small size of these cations is believed to prevent their substitution in most silicate structures. Hexagonal rings made up by six Si-O tetrahedra are the dominant feature of the crystal structure. The arrangement of the silica tetrahedral results in the formation of channels that are joined laterally by Al^{3+} and Be^{2+} ions. The channels can accommodate a range of impurity molecules such as water, CO_2 methane and impurity ions, such as $\text{Fe}^{2+/3+}$ and alkali ions. The enormous multitude of possible impurities and their combinations in emerald has made it subject to many spectroscopic investigations over the last six decades (Wood and Nassau 1968).

In our recent work we have mostly concerned ourselves with the properties of Cr^{3+} in natural and lab-grown emerald with the goal of gaining a better understanding of the electronic properties of this ion in D_3 symmetry plus its interactions with other impurities. The range of samples we investigated included natural emeralds from Brazil, Africa and Australia and lab-created pale green and nominally chrome-free emeralds from Chatham.

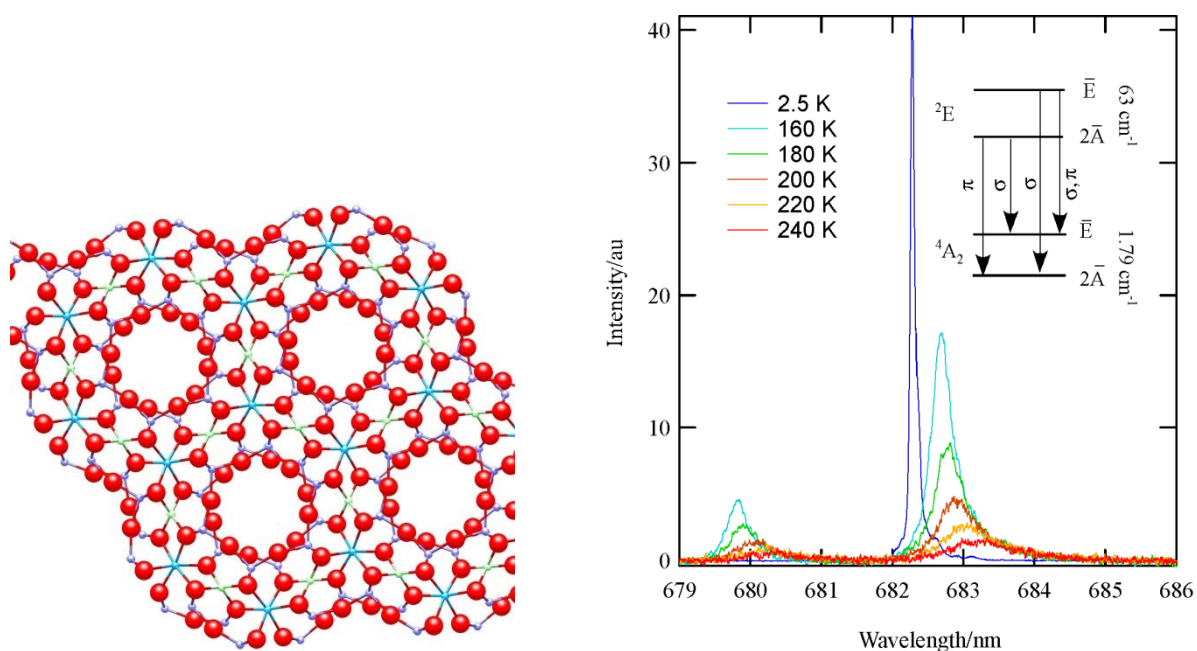


Fig. 1. Left, the crystal structure of beryl projected on the basal plane (0001) (red: O; green: Be; light blue: Al; purple: Si). Right, temperature dependence of the non-selectively excited luminescence spectrum of $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}:\text{Cr}^{3+}$ (0.0017%) (different gains were on the PMT were used).

In the present contribution we will present a brief introduction to selective laser spectroscopy and summary of experiments that we have conducted on these samples over the years. These experiments include luminescence and excited state lifetime measurements, Fluorescence Line Narrowing (FLN), transient and persistent spectral hole-burning (SHB) and, most recently, slow light experiments (Hayward and Riesen 2005; Riesen 2003; Riesen 2011). For example, we have found that the excited state lifetime varies significantly depending on the Cr^{3+} concentrations and the presence or absence of other impurities. This also applies to the inhomogeneous width of the R-lines as observed in low temperature luminescence and absorption spectroscopy and the efficiency of persistent spectral hole-burning. In addition, we have conducted a full investigation into the temperature dependence of the homogenous line width by employing FLN, SHB and luminescence spectroscopy. From a study of African emerald we have been able to conclude that the mechanism for persistent spectral hole-burning is intimately related to the presence of Fe^{2+} ions; a photoinduced electron transfer that is followed by a rapid back transfer in the electronic ground state slightly reorganizes the local environment of the Cr^{3+} impurity, yielding a relatively efficient photophysical hole-burning mechanism. Laser-based spectroscopy can be highly advantageous in the elucidation of complex electronic properties and behaviour of impurity ions in minerals, and can be used to characterize minerals and their origin and genesis.

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